

Edge effects in finite elongated carbon nanotubes

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The importance of finite-size effects for the electronic structure of long zigzag and armchair carbon nanotubes is studied. We analyze the electronic structure of capped (6,6), (8,0), and (9,0) single walled carbon nanotubes as a function of their length up to 60 nm, using a divide and conquer density functional theory approach. For the metallic nanotubes studied, most of the physical features appearing in the density of states of an infinite carbon nanotube are recovered at a length of 40 nm. The (8,0) semi-conducting nanotube studied exhibits pronounced edge effects within the energy gap that scale as the inverse of the length of the nanotube. As a result, the energy gap reduces from the value of ~ 1 eV calculated for the periodic system to a value of ~ 0.25 eV calculated for a capped 62 nm long CNT. These edge effects are expected to become negligible only at tube lengths exceeding $6 \mu\text{m}$. Our results indicate that careful tailoring of the nature of the system *and* its capping units should be applied when designing new nanoelectronic devices based on carbon nanotubes. These conclusions are expected to hold for other one-dimensional systems such as graphene nanoribbons, conducting polymers, and DNA molecules.

Carbon nanotubes (CNTs) have been suggested as potential candidates for replacing electronic components and interconnects in future nanoelectronic devices.¹ Experiments have revealed the possibility of obtaining a wide range of electronic behavior when studying these systems, ranging from coherent transport^{2,3} suitable for interconnects, to field effect switching capabilities^{4,5,6,7} needed for electronic components design. While earlier conductance experiments^{2,3,4,5,6,7,8,9} involved long segments of CNTs, new technologies allow for the fabrication of ultrashort CNT junctions where reproducible room temperature ballistic transport at the high bias regime is observed.^{10,11} Nevertheless, the reduced length of the CNT junctions, which is essential to suppress electron-phonon scattering, introduces important physical phenomena such as quantum confinement and edge effects. Several theoretical studies have emphasized the importance of such effects when considering the electronic structure,^{12,13,14} electric transport,^{15,16,17,18,19} and magnetic^{20,21,22} properties of finite CNTs. These effects are expected to be manifested in experiments involving the dielectric screening constants,²³ optical excitations²⁴ and the Raman spectroscopy²⁵ of such systems. Since it is predicted that the physical characteristics of *finite* CNTs are considerably different from those of their *infinite* counterparts, it is essential to identify the limit at which finite size effects have to be taken into account in order to properly describe their electronic properties.

Therefore, a fundamental question arises: Is there a universal CNT length below which finite size effects become important? The aim of this Letter is to answer this question. To this end, we present a novel density functional theory (DFT) study of the electronic structure of CNTs as a function of their length, up to 62 nm. Using a divide and conquer approach for first-principles electronic structure and transport calculations through finite elongated systems,²⁶ we study the finite size effects on the electronic structure of capped (6,6), (8,0), and (9,0) CNTs. A careful comparison with the electronic

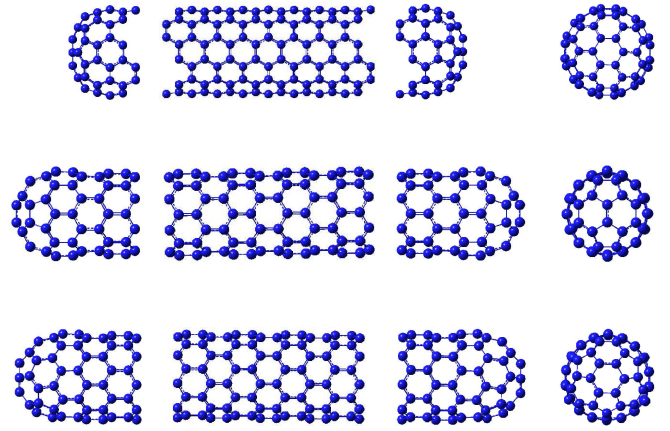


FIG. 1: Optimized geometries of a (6,6) (upper panel), (8,0) (middle panel), and (9,0) (lower panel) CNTs. Shown are side views of the left capping end, right capping end, and the central part which can be replicated to produce the finite elongated system. An axial view of one of the caps of each CNT is depicted on the right.

structure of infinitely long periodic CNTs enables us to determine the limit at which a finite CNT can be fairly approximated by its infinite periodic counterpart.

Our results show that for the metallic CNTs studied herein, most of the physical features appearing in the density of states (DOS) of the infinite periodic system are recovered at a length of 40 nm. A similar picture arises for the semi-conducting CNT considered. However, a subtle difference exists. Pronounced features in the DOS resulting from edge effects appear at the vicinity of the Fermi energy, thus substantially influencing the electronic character of the CNT. These features are expected to abide up to CNTs lengths of $60 \mu\text{m}$, much longer than previously predicted.¹⁶

The relaxed structures of the CNTs employed in this study are presented in Fig. 1. These configurations have

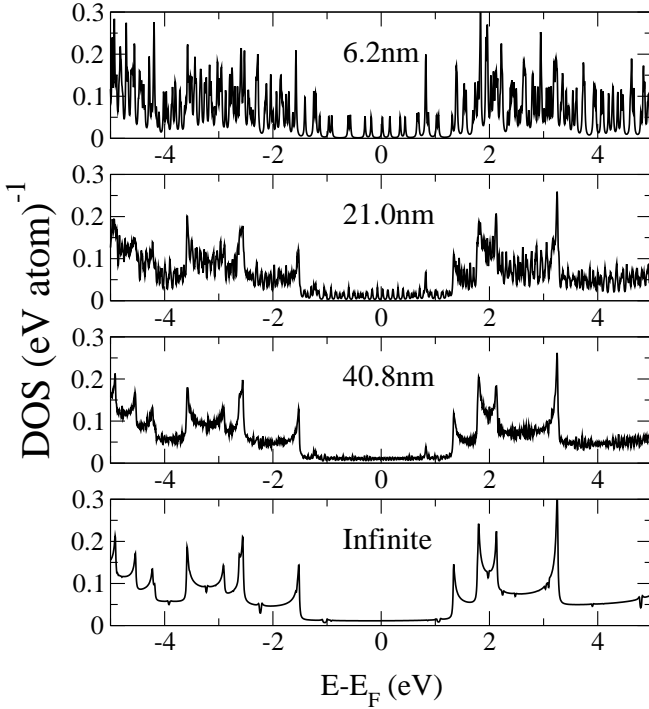


FIG. 2: Density of states of a capped (6,6) CNT calculated for several tube lengths and compared to the DOS of the periodic system (lower panel). The energy axis origin of all the panels is set to the Fermi energy of the periodic system (-4.42 eV)

been obtained using Pople's Gaussian basis set^{27,28} and the Perdew-Burke-Ernzerhof^{29,30} realization of the generalized gradient approximation of density functional theory as implemented in the *Gaussian* suite of programs.³¹. The DOS calculations has been carried out using the following relation:

$$\rho(E) = -\frac{1}{\pi} \Im \{ \text{Tr}[G^r(E)S] \}, \quad (1)$$

where, S is the overlap matrix, $G^r(E) = [\epsilon S - H]^{-1}$ is the retarded Green's function (GF), $\epsilon = E + i\eta$, E is the energy, H is the Hamiltonian matrix, and $\eta \rightarrow 0^+$ is a small imaginary part introduced in order to shift the poles of the GF from the real axis. The Hamiltonian matrix is calculated using a divide and conquer DFT approach.²⁶ Within this approach H is represented by a block tridiagonal matrix, where the first and last diagonal blocks correspond to the two capping ends of the CNT. The remaining diagonal blocks correspond to the central part of the CNT which is composed of a replicated unit cell. The two capping ends and the replicated central part unit cell are chosen to be long enough such that the block-tridiagonal representation of H (and S) is valid. All the electronic structure calculations are performed using the screened exchange hybrid functional of Heyd, Scuseria, and Ernzerhof³², that was found to provide a good description of the single-particle band energies of

both semi-conducting³³ and metallic³⁴ CNTs. The capping end diagonal Hamiltonian blocks and their coupling to the central part are evaluated via a molecular calculation involving the two capping ends and one unit cell cut out of the central part. We approximate the central part replicated unit cell blocks and the coupling between two such adjacent blocks to be constant along the CNT and extract them from a periodic boundary condition³⁵ calculation. The resulting block-tridiagonal matrix $(\epsilon S - H)$ is then partially inverted, using an efficient algorithm,³⁶ to obtain the relevant GF blocks needed for the DOS calculation. For a detailed description of our divide and conquer approach see Ref.[26].

In Fig. 2 we present the DOS of the (6,6) metallic CNT at an energy range of ± 5 eV around the Fermi energy of the infinite system for several tube lengths. Qualitatively, it can be seen that for a 6.2 nm CNT (upper panel) the DOS is composed of a set of irregularly spaced energy levels and is totally uncorrelated with the DOS of the infinite CNT (lower panel). As the length of the CNT is increased the agreement between the DOS of the finite and the periodic systems increases. At a length of 21 nm one can clearly see the buildup of the Van-Hove singularities and the constant DOS at the vicinity of the Fermi energy. When the length of the CNT exceeds 40 nm, finite size effects become negligible and most of the physical features appearing in the DOS of the infinite system are recovered. A similar behavior is obtained for the DOS of the metallic (9,0) CNT (not shown).

In order to quantify these results we apply a linear cross-correlation analysis utilizing Pearson's formula.³⁷ In short, given two discrete data sets X_i and Y_i , where $0 \leq i \leq M$ one can calculate their cross-correlation as follows:

$$r = \frac{\sum_i [(X_i - \bar{X})(Y_i - \bar{Y})]}{\sqrt{\sum_i (X_i - \bar{X})^2} \sqrt{\sum_i (Y_i - \bar{Y})^2}}. \quad (2)$$

Here r is Pearson's cross-correlation factor, \bar{X} is the mean value of the X_i data set, and \bar{Y} is the mean value of the Y_i data set. The cross-correlation factor of Eq. 2 is normalized such that $-1 \leq r \leq 1$. When $r = 1$ the two sets are completely correlated, when $r = -1$ one set is completely correlated with the inverse of the other set, and when $r = 0$ there is no significant correlation between the two sets.

In Fig. 3 we show the calculated cross-correlation factor between the DOS of the finite CNTs and that of the infinite counterparts as a function of the tubes lengths. For the shortest CNTs studied, the calculated Pearson's factor indicates no correlation of the DOS to that of the periodic system. As discussed above, when the length of the CNT is increased, the electronic structure of the infinite system is recovered. This translates to an asymptotic Pearson's factor value of $r = 1$.

A natural question is: At what length can an infinite metallic CNT be used in order to represent the electronic structure of its finite counterpart? The answer to this

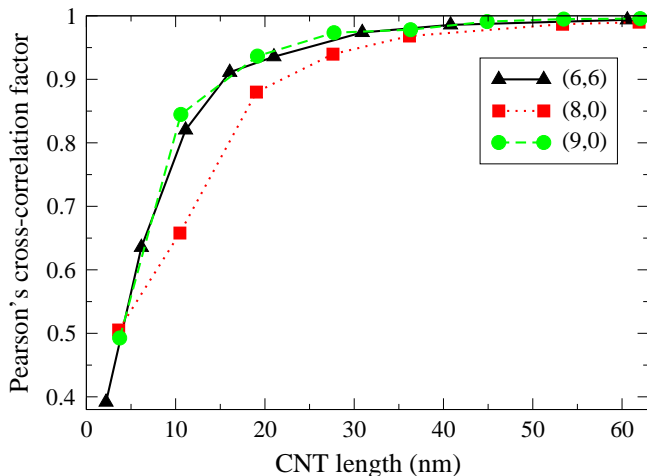


FIG. 3: Pearson's cross-correlation factor between the DOS of finite and periodic (6,6) (solid black line), (8,0) (dotted red line) and (9,0) (dashed green line) CNTs as a function of the finite CNTs lengths.

question depends, of course, on the specific type of metallic CNT and on the nature of the electronic properties considered. For metallic CNTs one can identify (at least) two important features in the DOS, namely the *Van-Hove singularities*, which are manifested as characteristic signatures in the optical spectra of CNTs, and the *finite DOS* at the vicinity of the Fermi energy which accounts for the metallic character of the CNT. From a careful analysis of the DOS plots we find that the Van-Hove singularities are fairly recovered at a length of ~ 35 nm for both metallic CNTs considered. The buildup of a finite DOS at the vicinity of the Fermi energy is achieved at a slightly larger length of ~ 45 nm. This is also reflected in the computed Pearson's cross-correlation factor that is as high as $r = 0.98$ at these CNTs lengths (see Fig. 3).

We now turn to discuss the semi-conducting CNT. Similar to the metallic case, we consider the Van-Hove singularities and the energy band gap (E_g) as two important characteristic features of its DOS. The reconstruction of the Van-Hove singularities as the length of the finite semi-conducting CNT is increased, follows the same lines described above for the metallic case. Nevertheless, a subtle difference exists. In Fig. 4 the DOS of the finite (8,0) capped CNT is presented for several CNT lengths at a region of ± 0.75 eV around the Fermi energy of the infinite periodic system. While E_g of an infinite periodic (8,0) CNT is calculated to be 1 eV (lower panel of Fig. 4), even for the longest CNT considered (~ 62 nm), a noticeable DOS pattern clearly appears within the energy gap region, thus reducing the effective gap to a considerably lower value of 0.25 eV. These states are identified as edge effects which originate from the capping units of the finite CNT. Their appearance also translates to a slower approach of the cross-correlation factor towards its asymptotic value, as can be seen in Fig. 3.

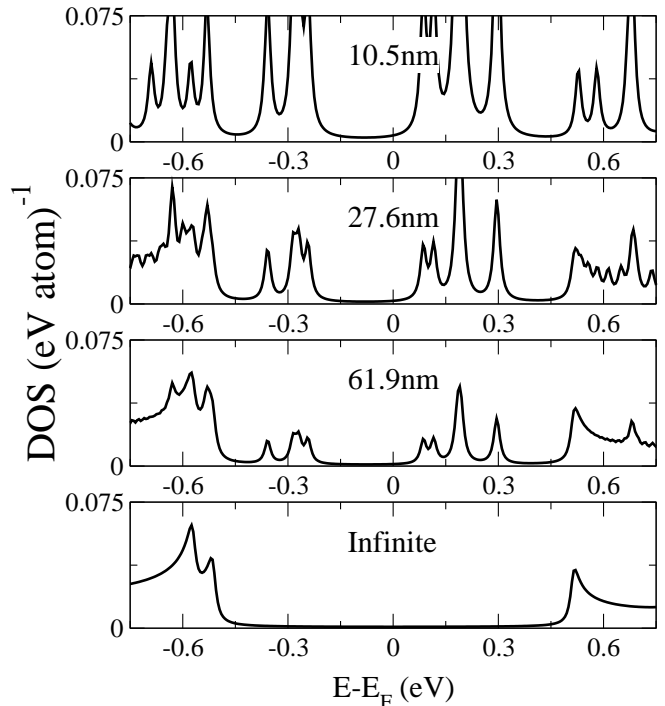


FIG. 4: Density of states of a capped (8,0) CNT calculated for several tube lengths and compared to the DOS of the infinite periodic system (lower panel). The energy axis origin of all the panels is set to the Fermi energy of the infinite CNT (-4.53 eV)

At this point, it should be mentioned that in order to obtain the DOS diagrams we have artificially broadened the energy levels by a value of 1×10^{-2} eV. In an experimental setup this may correspond to broadening due to electron-phonon coupling, surface/contacts effects, and finite temperature effects. In order for the edge effects to become negligible it is desired that their peak DOS value would be considerably smaller than the height of the broadened Van-Hove singularities corresponding to the top of the valence band and the bottom of the conduction band. The height of the edge-related peaks scales roughly as $\sim 1/L$, where L is the length of the finite CNT. For the broadening value mentioned above, a CNT length of $\sim 6 \mu\text{m}$ is needed for the peaks to become less than 1% in height with respect to the van-Hove singularity appearing at the bottom of the conduction band (located ~ 0.5 eV above the Fermi energy). This value is much larger than the typical CNT length used in many experimental setups, which implies that the inclusion of quantum confinement and edge effects can become crucial for the appropriate interpretation of experimental results. It should be noted that the nature of the edge-related DOS peaks appearing within the energy gap depends on the characteristics of the capping units. Other systems with different capping units may exhibit different features.

Edge effects play a dominant role when considering the electronic and magnetic character of low dimensional elongated systems. This has been shown for systems such as graphene nanoribbons,^{38,39,40,41} carbon nanotubes,^{12,13,14,15,16,17,18,19,20,21,22} and other related structures.⁴² When considering the study of carbon nanotubes as candidates for future nano-electronic devices, it is important to identify the contribution of finite size effects to the physical properties of the entire system. In the present letter, we have shown that the limit at which finite-size effects become negligible, highly depends on the system under consideration, the capping units, and the physical property of interest. This has been done by studying the DOS of CNTs as a function of their length and comparing with that of the periodic system. Our results suggest that for the metallic systems studied, a CNT segment of, at least, 40 – 60nm has to be considered if edge effects are to be neglected. For the semi-conducting CNT studied here, prominent edge effects are expected to dominate up to lengths as high as a few microme-

ters. Even though the exact details of such effects are expected to depend on the nature of the capping units, care should be taken regarding their influence on the electronic character of the system. Our conclusions should hold for other finite elongated systems such as graphene nanoribbons, conducting polymers, and DNA molecules, as well. More research along these lines is currently in progress.

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